IJBST

ISSN: 0974 – 3987
IJBST (2014), 7(2):5-14

Plasma-Chemical Inactivation of Bacteria

Jean-Louis Brisset[1], Eugen Hnatiuc[2], Bogdan Hnatiuc[3] and Georges Kamgang Youbi[4]
1 Prof. Em. Faculty of Sciences; University of Rouen ; Mont St -Aignan 76821, FRANCE
2 Prof. Gh. Asashi Technical University; Blvdu Mangeron 51-53 , Iasi 700050, ROMANIA
3 Assistant Prof. Maritime University, Constanta, ROMANIA
4 Lecturer Mineral chemistry Laboratory, University of Yaounde-I. Yaounde, CAMEROON
brissjl@club-internet.fr

ABSTRACT:
Electrical discharges at atmospheric pressure are a developing source of inactivating species efficient for organic pollutants abatement and sterilization. A rapid analysis of the active species formed in a gliding arc in humid air ("glidarc"), such as °NO and °OH radicals, shows that these Reactive Oxygen and Nitrogen Species are directly or indirectly (by means of their derivatives) responsible for the oxidizing and acidifying chemical effects in aqueous solutions exposed to the discharge. The standard oxidation potentials of °OH/H_2O and its associated dimer H_2O_2/H_2O are respectively 2.85 and 1.78 V/SHE. °NO is implied in a set of reactions leading to the formation of Reactive Nitrogen Species, e.g., peroxynitrite, as another water soluble intermediate and a precursor for nitric acid. The standard oxidation potential of $ONOO^-/NO_2$ is higher than $E°(H_2O_2/H_2O)$, so that this system may be actually considered as a determining agent in inactivating processes of bacteria. Matching kinetic studies concerning Gram positive and negative bacteria directly exposed to the plasma show that the inactivation kinetics involve a pseudo zero order step followed by a diffusion controlled pseudo first order step. Temporal Post-Discharge Reactions also take place after switching off the discharge, which confirms the occurrence of active plasma species in the liquid, probably H_2O_2 and $ONOOH/ONOO^-$, in agreement with Biochemistry studies on the peroxynitrite degradation of bacterial wall components (e.g., lipoproteins or teichoic acid, after splitting into °OH and ONO^-). Peroxynitrite was also found responsible for the degradation of nucleic acid, and therefore for the lethal effect of plasma treatment of bacteria. The newly confirmed effect of Plasma Activated Water" on inactivating bacteria is a strong argument in favour of plasma species incorporated into aqueous media.

Keywords: Bacterial Inactivation; Gliding Electric Discharge in Humid Air; Reactive Nitrogen Oxygen Species; Peroxynitrite; Post-discharge.

INTRODUCTION

An overlook on plasmas

The commonly used definition for a plasma is a gaseous mixture of electrons, photons and heavy species (i.e., ions, molecules, radicals and atoms) in the energy ground state or/and raised to some activated state by energy exchange with a suitable source.Convenient sources may be man-made (e.g., flames, explosions), mechanical (e.g., shock waves, ultrasound), or electromagnetic (e.g., electric or magnetic fields, lasers) or natural (e.g., lightnings, polar lights). The formed plasmas are classified into "thermal" and "non—thermal", according to the occurrence ofa thermic(and thermodynamic)local equilibrium (TLE) between electrons and heavy species. Figure 1 illustrates the usual distribution between cold and thermal plasmas.

The thermal plasmas operated at high pressure (i.e., atmospheric pressure or higher) concern torches, arcs and explosions: the high local temperature favours thermal treatments as for metallurgy processes but is completely unadapted in case of pollutant abatement of liquid wastes and environmental applications. We also discarded non- thermal plasmas (e.g., low pressure plasmas) because liquids vapourize in these conditions. Fortunately, a group of plasma techniques exists at low temperature, close to room temperature and high pressure which are sometimes referred to as "tepid" plasmas. They involve corona, dielectric barrier, glow discharges and a particular system, i.e., the gliding arc [1] which is a *quenched* thermal plasma (arc) with very limited thermal effects, but a rather important population of present active species. The governing working parameters, i.e., the applied voltage and the current average intensity, are joined together in the U vs. I plot [2] which also illustrates the discharges sharing between thermal and non-thermal (Fig.2).
We are concerned with the chemical properties of the discharges and the relevant applications of the "glidarc" discharge to solving environmental problems, e.g, the degradation of organic wastes, persistent molecules, spent solvents and more recently, bacterial inactivation.

Electrical discharges, e.g., corona, dielectric barrier and gliding discharges are thus known sources of non-thermal plasma at atmospheric pressure. When they burn in humid air, i.e., in a mixture of N_2, O_2 and H_2O molecules, these discharges generate active species such as °NO and °OH radicals, which are identified and quantified by emission spectroscopy. These key species are responsible for most physical-chemical effects of the plasma treatments, i.e., the oxidizing and acidifying effects, when they are in contact with (non-buffered) aqueous solutions. The gliding arc ("glidarc") discharge is probably the most illustrative example of plasma-chemical application, due to the large amount of energy carried away and transferred to the ambient gas, and the matching high production of active species.

The gliding arc ("Glidarc")

The gliding arc was proposed by Lesueur et al [3] at the end of the eighties and developed by Czernichowski et al. [1,4] for gas treatment and

gaseous pollutants abatement. It was later adapted to the treatment of liquids and solutes [5].

The glidarc forms at the minimum gap between two diverging electrodes connected with a suitable High Voltage source, e.g., a HV transformer (50 Hz; 9000V; 160 mA in usual working conditions). The arc which is a thermal plasma is pushed along the electrodes to their tips by a humid air flow directed along the reactor axis. When the arc is short-circuited by a new one and breaks, a quenched non-thermal plasma cloud forms, with a composition close to the arc but a temperature by few degrees higher than room. The aqueous target solution is disposed in front of the gas flow in a cooled vessel to limit evaporation (Fig. 3, right), so that the plasma species are in contact with the organic species present at the liquid surface or dispersed in the bulk liquid. Some devices use an injection nozzle for both the aqeous target as droplets and the input gas.

Chemical properties of the plasma species

The high energy concentration associated with discharges induces strong interaction with the surrounding gas and leads to excitation, bond breaking and ionization of the molecules. Hydroxyl radicals mainly result from electron impact at excited H_2O molecules, with the matching formation of O atoms which are also yielded by breaking the O-O bonds [6].

The electron channel of the arc passing through humid air generates excited O atoms that are able to dissociate N_2 molecules by direct impact, according to the set of endoergic reactions governing the Birkeland-Eyde process for nitric acid preparation:

$$O_2 + e^- \rightarrow 2\,O^\circ + e^- \quad [1]$$
$$N_2 + O^\circ \rightarrow {}^\circ NO + N^\circ \quad [2]$$
$$N^\circ + O^\circ \rightarrow {}^\circ NO \quad [3]$$

°NO is then able to fix an O atom provided by any available O-donor moiety (e.g., $^\circ O_2H$, O_3 …) and yields the bent °ONO radical. Nitrogen dioxide then enters a set of complex reactions developed elsewhere [5-7]. °NO is thus the source of transient nitrous ONOH [pK_a(ONOH/ONO^-) = 3.3] and peroxynitrous ONOOH acids [pK_a (ONOOH/$ONOO^-$) = 6.8]; isomerization of linear ONOOH later takes place and yields stable, trigonal and nitric acid ($H^+ + NO_3^-$). Such feature accounts for the observed pH lowering of non-buffered solutions.

The standard oxidation potentials of the systems °OH/H_2O and its associated dimer H_2O_2/H_2O with water are respectively 2.85 and 1.78 V/SHE. °NO is thus implied in a file of complex reactions [6,7] which lead to the formation of Reactive Nitrogen Specie (RNS) such as peroxynitrite as another water soluble intermediate and a precursor for nitric acid [5-8]. The standard oxidation potentials of the systems $ONOO^-$/ NO_2 and ONOOH/NO_2 are higher than that of the H_2O_2/H_2O system, respectively 2.44 V/SHE and 2.05 V/SHE: such a feature shows that peroxynitrite may be actually considered as a determining agent in organic compounds degradation and inactivating bacteria processes. Peroxynitrite is claimed to oxidize lipids, proteins and lipoproteins, a feature which induces the breaking of molecular bondings and therefore serious damage on bacterial membranes [7,9,10]. Many Biology studies admit that the compound is implied in molecular stress and able to react with components of the bacterial membranes; other works claim that it is directly concerned with the development of deseases, such as Alsheimer's. Biologists' works also show that peroxynitrite is able to split into ONO^- and °OH and participate to hydroxylation, nitration and nitrosation reactions [13], as illustrated by Figures 4 and 5, additionally to the nucleophilic character evidenced by the reaction with carbon dioxide [12]. The dissociation into NO^+ and O_2H^- also agrees with the observed nitrosation/ nitration reactions .

Space distribution of active species in a gliding arc discharge

Figure 6 illustrates the distribution of the main species formed in gliding discharges [6]. The “Parent species” refer to the the gas molecules at the reactor input, i.e., O_2, N_2 and H_2O. The hydroxyl radicals result from electron impact at the H-OH molecules and implies electrons in the core of the electron channel, as well as O atoms, ions and various excited species. In particular, the largely endoergic dissociation of N_2 probably takes place in the arc or at its immediate surrounding and involve the slower electrons that tend to escape from the electron channel. These “Primary species” then react both among them and with Parent species in the plasma cloud and yield “Secondary species” (e.g., NO, NO_2, or the dimer H_2O_2). The resulting Primary and Secondary species impinge at the liquid surface and react with the target molecules present. They can also solubilize in water because H_2O_2 and ONOOH are water soluble and diffuse in the liquid phase before reacting with the solutes or the dispersed species.

CHEMICAL EFFECTS OF ACTIVE SPECIES ON ORGANIC SOLUTES

Organic pollutants abatement

The chemical properties of the active species formed in a discharge were first used for organic wastes destruction. The applications concern a large pannel of compounds ranging from spent industrial solvents, such as toluene, ethyl acetate, 2-propanol or ethyleneglycol [14 -15] or halogen containing hydrocarbides [16], to persistent molecules, such as laurylamine, trilaurylamine or tributylphosphate used in the Purex Process in nuclear reprocessing industry or other P-containing warfare agents [17-19]. Numerous examples of dye bleaching or degradation are available in the literature with or without catalysts such as TiO_2 [20-25]. The glidarc technique was also

successfully applied to pollutant abatement of domestic, urban and workshop organic wastes [26-30] and various typical molecules such as hemoglobin [31], as illustrations for both Iron complexes and compounds of biological interest.

Bacterial inactivation

The large and diversified experience acquired in the glidarc treatment of organic wastes [5, 14-31] led us to consider bacteria, yeasts, moistures and mushrooms as particular forms of organic materials. Hence the organic pollutant abatement observed enven for persistent molecules let us think that plasma-chemical treatments might be successful in case of living matter [32-35; 37-40]. Since these targets are scarcely "soluble" in water, we considered that they were actual aggregates dispersed in the liquid. Hence, the plasma species should intact with bacteria both at the liquid surface, in the same way as for surfactants, and in the bulk solution. For the second case we guessed that the plasma active species (soluble ROS/RNS) and the bacteria diffuse in the solution, and that the inactivation reactions take place at the external membrane of the bacteria by mere chemical effect.

1. Lethal effects

Bacterial colonies exposed to a gliding discharge burning in humid air are severely damaged up to their death, whatever may be the physiological state of the treated bacteria (planktonic, adherent, detached states or even spores).

The examined bacteria are selected among Gram positive and Gram negative bacteria, e.g., *St. epidermidis, Leuconostoc mesenteroides*, as well as *E. coli, Erwinia carotovora, Hafnia alvei* respectively or *fecal coliforms* and *streptococci* present in industrial effluents of African tanning workshops [29]. Bacterial inactivation resulted also of the plasma-chemical treatment of sulfato-reductive and thiosulfato-reductive bacteria. Same preliminary positive results were observed for mushrooms and moistures.

Yeasts (e.g., *Saccharomyces cerevisiae*) were also exposed to the discharge and confirmed the inactivating effect of the plasma treatments.

2. Analytical methods

The analytical methods used for analyses were those employed in Microbiology laboratories. They mainly consist in plating, i.e., in counting the number of colony forming units (CFU) per mL on gelose plates, according to standard procedures. The CFU results were the mean values of three sets of independent experiments.

Scanning Electron Microscopy of 5 min treated *Erwinia* (Fig.7) shows serious damage at the external surface of the bacteria. These observations suggests the occurrence of an "etching effect", as guessed by Lerouge et al. [34].

However pictures of other plasma-treated bacteria invalidate this assumption [35] but not that of a chemical action of the plasma species on the bacterial membrane components.

3. Bacterial membranes

The chemical stucture of the external membrane of Gram positive and negative bacteria is sketched in Figure 8. These structures involve several similar components whose formulas are illustrated in Figure 9.

Three key components of bacterial membranes [7]: Teïchoic acid (A), Lipopolysaccharide (B) and Peptidoglycan (C) are shown in Figure 9.

It can be underlined that Biologists's works demonstrated that proteins, sugars and lipids were sensitive to peroxynitrite. It is then reasonable to guess that this compound is directly concerned with the degradation of cells membranes.

Additionally, chemical analyses of proteins present at the membrane were titrated by the Bradford's method (and confirmed by biuret tests) for plasma-treated bacteria: they evidenced a maximum concentration for increasing exposure time t* to the discharge. Also, chemical analyses of the lipopolysaccharide (LPS) molecules released in the plasma treatment were performed by KDO (keto2-deoxy3-octonate) titration and showed a continuous decrease for increasing t*. These results confirm the assumption of a chemical attack of the plasma active species at the bacterial membrane surface. In particular they agree with the observed with the conversion of organic phosphate into phosphoric acid [18,19].

Life/Death tests were also achieved on various bacteria but were found not reliable, because the results did not fully agree with plating numeration. This tricky result is attributed to the destruction of the fluorescent dye incorporated in the solution for spectral measurement.

4. Inactivation kinetics

Bacterial inactivation kinetics performed by glidarc technique with *direct* exposure of the bacteria to the discharge usually present two steps, i.e., a pseudo zero-order step followed by a pseudo first order step, as presented in Figure 10. *Hafnia alvei* was selected as a typical example [33] to illustrate the kinetics of the plasma treatments which confirm the usually observed behaviour of organic wastes under plasma conditions.

The zero order step is attributed to the degradation by direct impinging of active species, i.e., the step is governed by the formation of these species in the gas phase, while the second step is governed by diffusion phenomena of active species in the liquid state.

Delayed inactivation also takes place with plasma-chemical inactivation and fits with previously observed "Temporal Post-Discharge Reactions" (TPDR) [5] which develop after having switched off the discharge and account for the action of plasma species dissolved in the solution.

Evolution of *H. alvei* CFU is illustrated by Figure 11 in case of TPDR conditions. The TPDR effect has also been observed for other bacteria and microwave cold plasma [33, 35-38].

The question: "How long these TPDR can be observed ?" is an excellent one, but no definite answer can be put forward. It seems that the post-discharge time t_{pd} during which simple molecules (e.g., phenols or "simple" dyes molecules are TPDR sensitive is much shorter than for heavy compounds. For example, TPDR effects last longer than 9 days [30] when hemoglobin from slaughterhouse is degraded in a circulating plasma reactor, and several weeks for the degradation of Alizarin Red Sulphonate in a batch reactor [36] .

The tricking evolution of KDO mentioned in section 2.2.3 is simply explained by the occurrence of TPDR. The membrane LPS is oxidized by the plasma species, such as peroxynitrite, so that the KDO is liberated by breaking the bond with LPS and its concentration increases in the treated solution, while it is itself degraded by the active species, leading to a continuous decrease.

Another consequence of TPDR, i.e., the incorporation of active species in the solution and their reaction with solutes, concerns the results published in numerous papers accounting for the degradation of organic dyes and indicators, and more generally of all organic chemicals incorporated in the plasma treated solutions in view of titration. This consequence means that a large number of published results are probably erroneous, although one can reasonably guess that only qualitative results are reliable as "instant" results but not as quantitative ones. In particular, this feature explains why life/death tests gave uncertain results, due to the degradation of the fluorescence dyes.

5. Super delayed inactivation process: Plasma Activated Water [7, 35, 37, 39, 40]

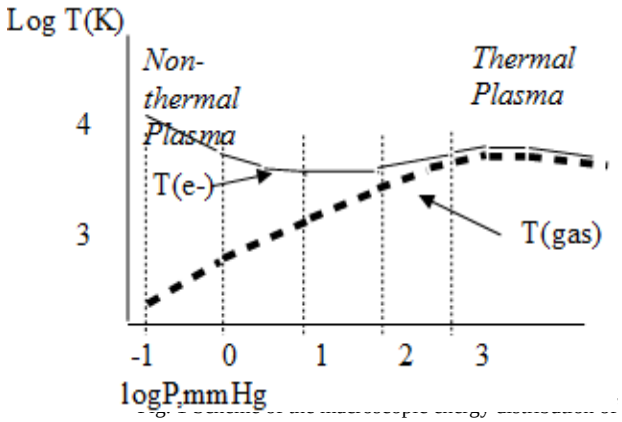
The occurrence of TPDR reactions was verified with numerous studies on organic wastes abatement, but was only recently confirmed in case of bacterial inactivation. This feature led Kamgang Youbi et al [35,37,39,40] to check new relevant consequences.

Assuming that inactivation reactions developed in the liquid and resulted from the solubilization of active species in water, it was found reasonable to test the inactivating ability of "plasma activated water".

Pure water was thus exposed to the glidarc for limited exposure times t* before checking the possible biocidal properties by incorporating bacterial cultures [7, 35, 37, 39]: bacterial inactivation was observed and the rate of the relevant pseudo first-order kinetics $k_{1,\,PAW}$ was measured [40] for various planktonic bacteria in contact for t_{PAW} with water previously exposed to the discharge for t*= 5 min (Fig 12).

The kinetic constants relevant to bacteria are of the same order of magnitude, except for the yeast. This feature may be tentatively considered as a positive argument in favour of the diffusion of plasma activated species, such as peroxynitrite, in the aqueous media.

The tricking biocidal properties of PAW were confirmed in a recent paper [40]. They require improved information but suggest that PAW is a powerful and cheap tool for cleaning and strerilizing.



electrons and gaseous species in terms of temperature.

IJBST

ISSN: 0974 – 3987
IJBST (2014), 7(2):5-14

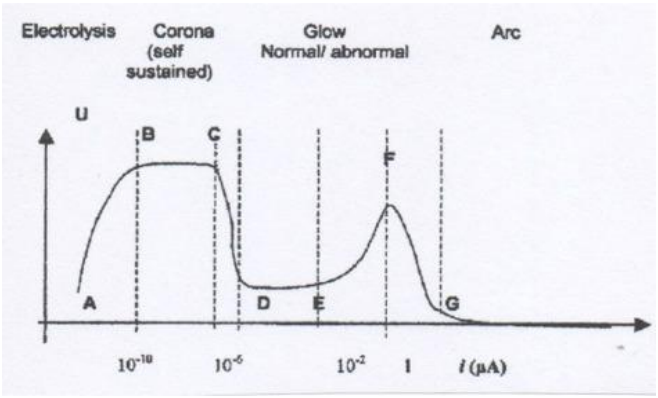


Fig.2 Caracteristic plot U vs I (Von Egel [2]) showing various domains: (AB) accounts for electrolysis phenomena; (BC) is relevant to self-sustained Townsend's discharges, illustrated by corona discharges; (CD) is a transition to the normal (DE) and abnormal (EF) glow discharges ranges; the domain (FG) is a transition to arc and that is where glidarcs usually operate. The higher intensity domain is that of arcs, for $i > i_G$

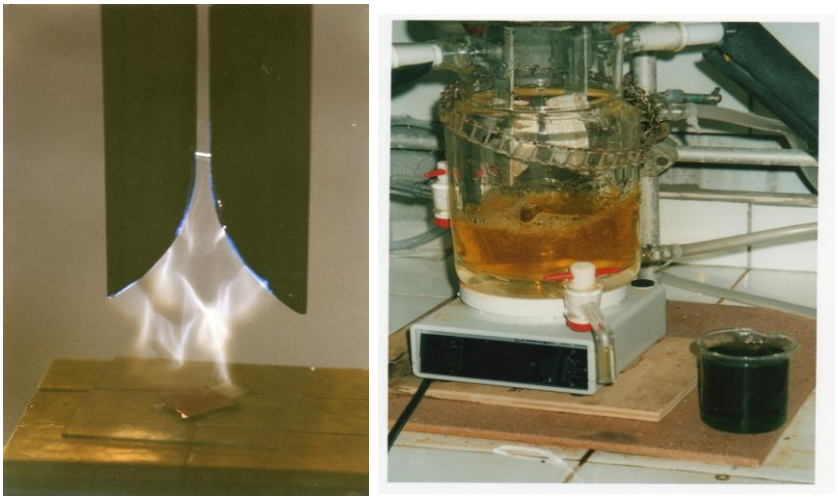


Fig. 3 Glidarc reactor:
Left: Detail of the electrodes for the treatment of Cu foils. Right: View of the reactor for batch treatments of liquids.(The energy source, a HV Transformer, is not shown. Specific energy : 500-700 JL^{-1}).

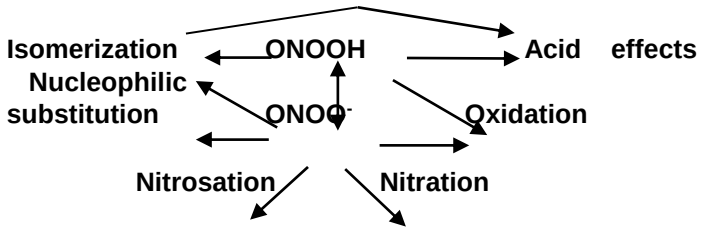


Fig. 4 Synoptic scheme of the ONOOH /$ONOO^-$ reactivity

ISSN: 0974 – 3987
IJBST (2014), 7(2):5-14

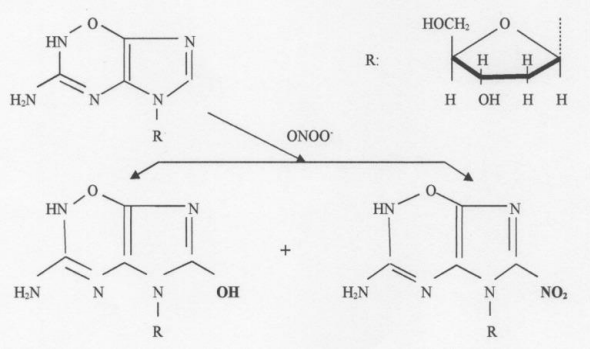


Fig. 5 Action of ONOOH on deoxyguanosine resulting of the splitting of the RNS reagent .

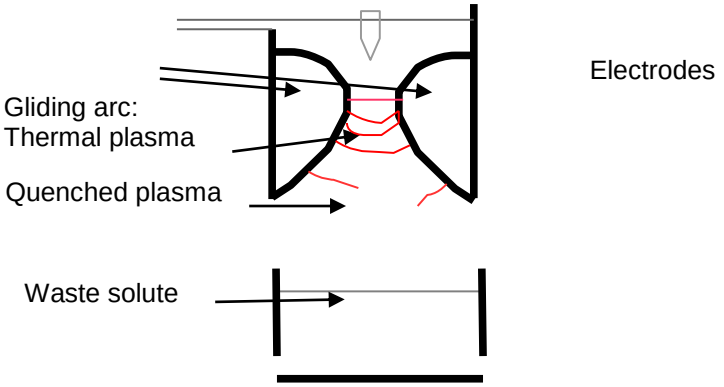


Fig. 6 Schematic distribution of the main reactive species in a glidarc reactor: Parent species O_2,N_2,H_2O (input gas); Primary species : H°,°OH, O°, H_2O*, N°, ions (arc); Secondary species: O_2^+, NO, NO_2, ONO^-, H_2O_2, HNO_3.
Liquid target: oxidation products, HNO_3, H_2O_2

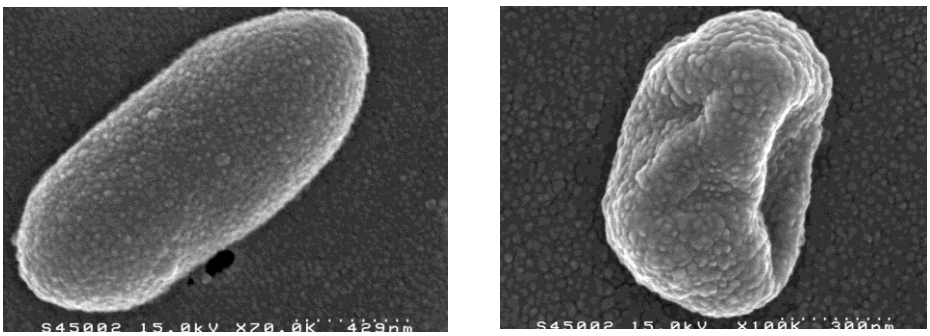


Fig. 7 *Erwinia carotovora atroseptica* 1526 directly exposed to the gliding arc for t*= 0 min (left) and for t* = 5 min (right) [32]. *Pictures by courtesy of Institut Micalis – BHM.*

ISSN: 0974 – 3987
IJBST (2014), 7(2):5-14

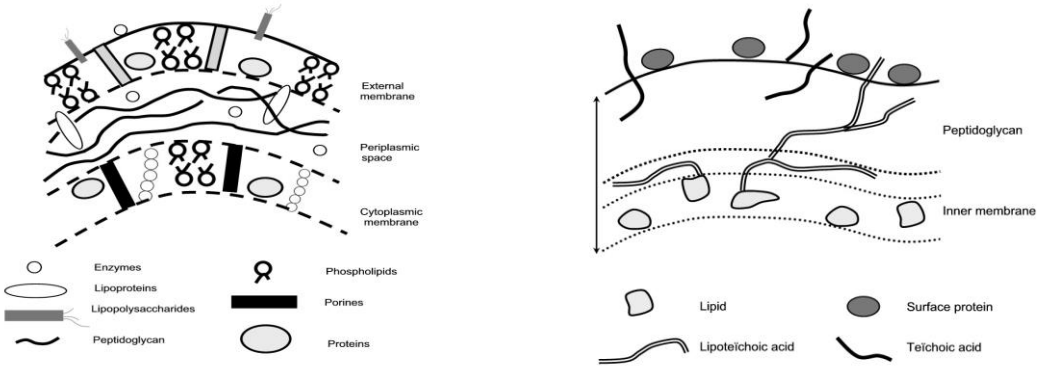


Fig. 8 Schemes of the external membrane structures of Gram negative (top) and Gram positive (foot) bacteria.

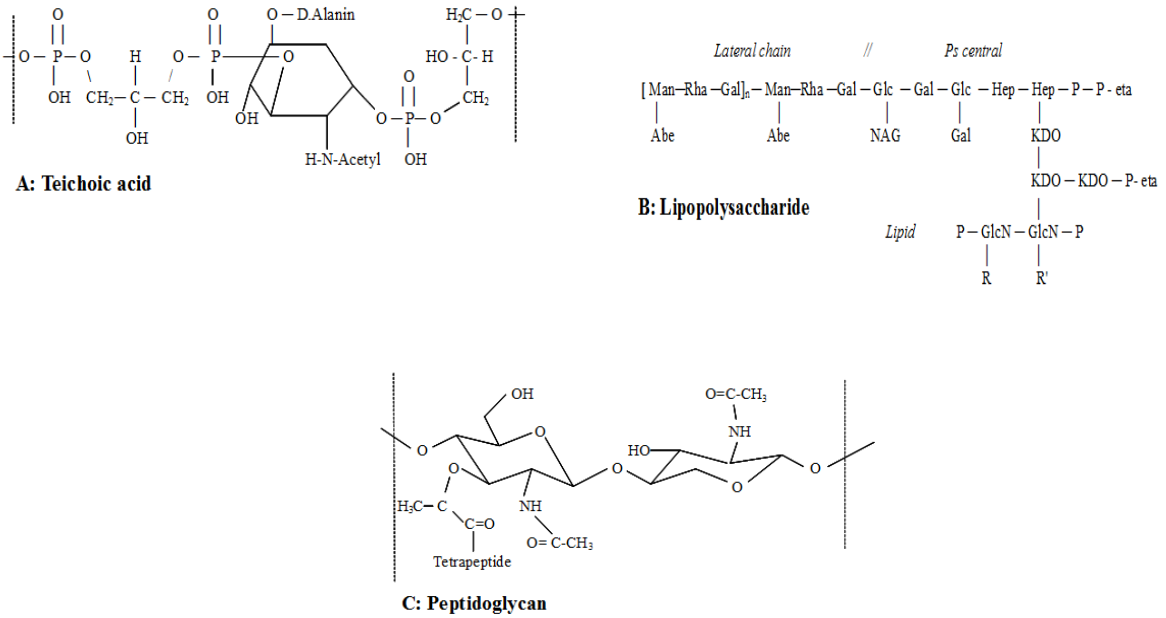


Fig. 9 Three main components of bacterial membrane: Teichoic acid (A), Lipopolysaccharide, LPS (B) and Peptidoglycan (C). [Abe: abequose; eta: ethanolamine; Gal: galactose; Glc :glucose; GlcN: glucosamine; Hep:heptulose; KDO: keto2-deoxy3-octanate; Man: mannose; NAG: N-acetylglucosamine; P: phosphate; Rha: rhamnose].

IJBST

ISSN: 0974 – 3987
IJBST (2014), 7(2):5-14

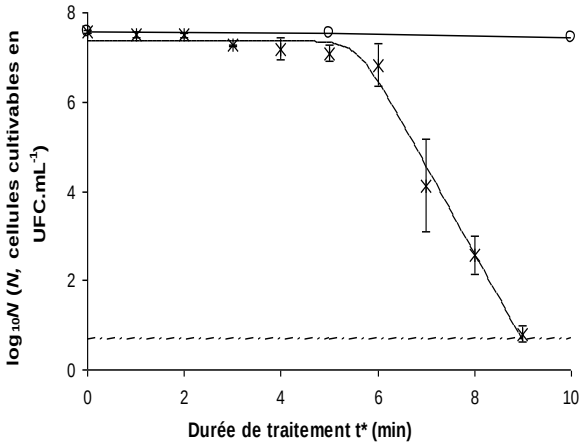


Fig.10 Inactivation of planktonic *Hafnia alvei* by direct exposure to the discharge for time t* (min) showing the evolution of $\log_{10}$ CFU as pseudo zero and first order kinetics and the detection threshold [39]

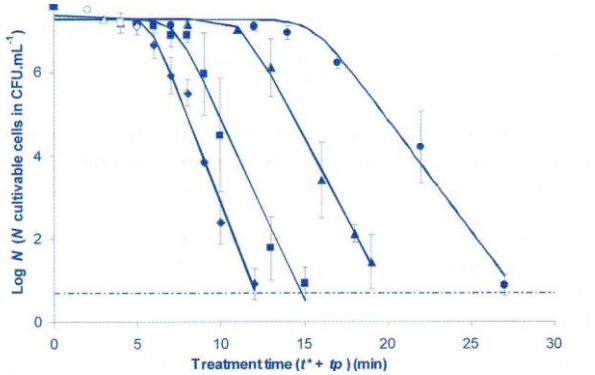


Fig. 11 Temporal Post-Discharge evolution of *H. alvei* [39] for various exposure times t* and relevant pseudo 1st order kinetic constants *k*, min^{-1}: *t**= 2min (black dots, *k* = 1.2)*; t*= 3 min triangles, k = 1.8); t* = 4 min (squares, k= 2.0); t*= 5 min (diamonds, k = 2.4).* Note that the *k* values linearly depends on t*.

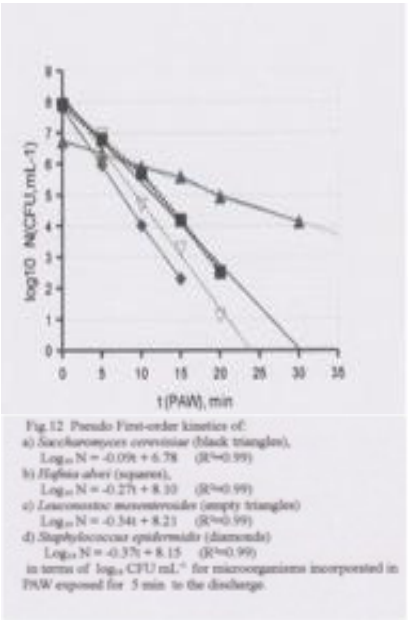


Fig.12 Pseudo First-order kinetics of:
a) *Saccharomyces cerevisiae* (black triangles),
$Log_{10} N = -0.098 + 6.78$ (R^2=0.99)
b) *Hafnia alvei* (square),
$Log_{10} N = -0.271 + 8.10$ (R^2=0.99)
c) *Leuconostoc mesenteroides* (empty triangles)
$Log_{10} N = -0.341 + 8.21$ (R^2=0.99)
d) *Staphylococcus epidermidis* (diamonds)
$Log_{10} N = -0.370 + 8.15$ (R^2=0.99)
in terms of log_{10} CFU mL^{-1} for microorganisms incorporated in PAW exposed for 5 min to the discharge.

CONCLUDING REMARKS

This study confirms that living materials are inactivated by exposure to gliding discharges in a two-step process, as organic wastes are degraded. Temporal Post-Discharge Reactions (TPDR) also take place and involve the diffusion of water soluble plasma species, i.e., Peroxynitrite and H_2O_2. The occurrence of TPDR is of key importance for further low cost application and above all explains the failure of Life/Death tests and the tricky results of chemical tests, e.g., KDO titration: the reagents and/or the dyes were oxidized by the plasma species. The post discharge effect is also confirmed by using Plasma Activated Water which appears as an interesting and unexpensive tool for cleaning operations.

ACKNOWLEDGEMENTS

This study was performed in the frame of the European COST Action TD 1028 “Electrical discharges with liquids for future applictions”.

A large part of the microbiology experiments was performed with *Institut Micalis*, AgroParisTech. (UMR-732 - BHM), 91744 Massy, France. We are largely indebt to our Colleagues Prof. M.-N. Bellon-Fontaine, Dr. M. Naitali, Dr. J.-M. Herry for fruitful discussion, and to our common student Dr. G. Kamgang Youbi, who implemented the experiments according to the Microbiology rules. GKY is particularly grateful to the Service d'Action Culturelle (French Embassy, Yaounde, Cameroon) for a grant.

REFERENCES

[1] Czernichowski A. (1994)- Gliding arc: Applications to Engineering and Environmental Control. - Pure Appl. Chem. 66: 1301-1310,

[2] Von Engel A. (1965) “Ionized gases”, Clarendon Press, p. 223.

[3] Lesueur H., Czernichowski A., Chapelle J. (1988) Dispositif de génération de plasmas basse température par formation de décharges electriques glissantes. - Fr. Patent 2 639 172, .

[4] Czernichowski A. (1993)- Gliding discharge reactor for H_2S valorization or destruction. In “Non-Thermal Plasma Techniques for Pollution Control” (B. Penetrante & S. Schultheis, Eds), NATO ASI Series Vol.G 34 B, Springer-Verlag, Berlin, pp. 371-387.

[5] Brisset J.-L., Moussa D., Doubla A., Hnatiuc E.,. Hnatiuc B., Kamgang-Youbi G., Herry J.-M., Naitali M., Bellon-Fontaine M.-N. (2008)- Chemical Reactivity of discharges and Temporal Post-Discharges in plasma treatment of aqueous media. Examples of gliding discharge treated solutions. A Review- Ind. Eng. Chem. Res. 47: 5761-5781 .

[6] Brisset J.-L., Hnatiuc E. (2012)- Peroxynitrite: a re-examination of the chemical properties of non-thermal discharges burning in air over aqueous solutions- Plasma Chem. Plasma Proces 32: 655-674.

[7] Naitali M., Herry J.-M., Hnatiuc E., Kamgang-Youbi G., Brisset J.-L. (2012)- Kinetics and bacterial inactivation induced by peroxynitrite by electric discharges in air - Plasma Chem. Plasma Proces 32: 675-692.

[8] Goldstein S., Squadrito G., Pryor W., Czapski G. (1996)- Direct and indirect oxidation mechanisms by peroxynitrite neither involving the hydroxyl radical- Free Rad. Biol. Med 21: 966-974.

[9] McConnell P., Reasor M., Van Dyke K. (2003)- Three model systems measure oxidation/nitration damage caused by peroxynitrite - J. Biol. Sci. 28: 71-76 .

[10] Squadrito G., Pryor W. (1998)- Oxidative chemistry of nitric oxide: the role of superoxide, peroxynitrite and carbondioxide - Free Rad. Biol Med 25: 392-403**.**

[11] D. Dobrynin, G. Fridman, G. Friedman, A. Fridman (2009)- Physical and biological mechanism of direct plasma interaction with living tissue - New J. Phys.11: 115020**.**

[12] O. Augusto, M. Bonini, A. Amanso, E. Linares, C. Santos, S. De Menezes (2002) - Nitrogen dioxide and carbonate radical anion : two emerging radicals in Biology- Free Rad. Biol. Med 32: 841-859.

[13] Radi R. (2004), Nitric oxide, oxidants and protein tyrosine nitration- *Proc. Nat Acad. Sci. USA.* 106.

[14] Tsagou-Sobze E. (2006) Application de decharges électriques à pression atmospherique dans l'air humide à la destruction de composés de haute toxicité et mise au point d'un dispositif de traitement pour des composés organiques volatils- Ph.D. Dissertation (in French); University of Rouen, France**.**

[15] Bellakhal N., Moras F., Boulay S., Desanaux C., Brisset J.-L. (2001)- Use of the gliding arc technique for pollution abatement of industrial wastes waters – Water, Waste and Environ. Res 2: 59-68.

[16] Estel L., Seguin D., Brisset J.-L.(1999)- Non-thermal plasma treatment for oxidation of halogenated organic molecules – Ann. New York Acad. Sci. 891: 199-206**.**

[17] Moussa D., Brisset J.-L., Hnatiuc E, Decobert G. (2006) - Plasmachemical destruction of trilaurylamine from nuclear reprocessing plants - Ind. Eng. Chem. Res 45: 30-33**.**

[18] Moussa D., Brisset J.-L. (2003)- Disposal of tributyl phosphate by gliding arc plasma - J. Hazard Mater. 102: 189-200.

[19] Pascal S., Moussa D., Hnatiuc E., Brisset J.-L. (2010) Plasmachemical degradation of Phosphorous containing warfare agents simulants - J. Hazard Mater. 175:1037-1041.

[20] Burlica R., Kirkpatrick M., Finney W., Clark R., Locke B. (2004). Organic dye removal from aqueous

solution by glidarc discharges- J. Electrostat. 62: 309-321.

[21] Abdelmalek F., Gharbi S., Benstaali B., Addou A., Brisset J.-L. (2004)- Plasmachemical degradation of azo dyes by humid air plasma : Yellow Supranol4GL, Scarlet Nylosan F3GL and industrial wastes- Water Res.38: 2339-2347.

[22] Moussa D, Doubla A., Kamgang-Youbi G., Brisset J.-L. (2007)- Post discharge long life intermediate in the plasmachemical degradation of an azo dye -IEEE Trans Plasma Sci. 35: 444-453.

[23] Laminsi S., Acayanka E., Teke Ndifon P., Djowe Tiya A., Brisset J.-L.(2012)- Plasmachemical dissociation and degradation of naphtol Green B complex – Environ. Eng. Manage. J. 11:1461-1466.

[24] Ghezzar M., Abdelmalek F., Belhadj M., Benderdouch N, Addou A. (2009)- Plasma degradation of textile wastewater by gliding arc discharge in the presence of TiO_2. - J. Hazard. Mater. 164: 1266-1274**.**

[25] Benstaali B., Bastaki N., Addou A., Brisset J-L. (2013)- Plasmachemical and photocatalytic degradation of methylorange - *Int. J. Env. Water Manage.* 11: 158-177**.**

[26] Njoyim-Tamungang E., Laminsi S., Ghogomu P., Njopwouo D., Brisset J.-L. (2011) - Pollution control of surface waters by coupling gliding electric discharges treatments with incorporated oyster shell powder - Chem. Eng. J. 173: 303-308.

[27] Mountapmbeme P., Acayanka E., Laminsi S., Brisset J.-L. (2012)- Degradation of palm oil refinery waste waters by nonthermal glinding arc discharge at atmospheric pressure- Env. Monit. Assessment**. (**doi: 10.1007/s10661-012-2984-3).

[28] Doubla A., Laminsi S., Nzali S., Njoyin E., Kamsu-kom J., Brisset J.-L.(2007)- Organic pollutants abatement and biodecontamination of brewery effluents by non-thermal plasma at atmospheric pressure- Chemosphere 69: 332-337.

[29] Laminsi S., Abba P., Tarkwa J., Djepang S., Brisset J.-L. (2014)- Non-thermal plasma decontamination of tanning workshop effluents from a tannery factory- Env. Eng Manage. J. , in press

[30] Gnokam Zumgang F., Doubla A., Brisset J.-L. (2010) Temporal Post-Discharges Reactions in plasma-chemical degradation of slaughterhouse effluents- *Chem. Eng.Comm.* 98: 483-493.

[31] Naitali M., Hnatiuc B., Herry J.-M., Hnatiuc E., Bellon-Fontaine M.-N., Brisset J.-L.(2009)- Decontamination of chemical and microbial targets using gliding arc discharges, Chap. 6 in "Biological and environmental applications of gas discharges" (G. Brelles Marino Ed.), Nova Science Publ. .

[32] Moreau M. (2006)- Decontamination bactérienne par décharge electrrique de tuype arc rampant dans l'air humide à tempétrature abiante et pression atmospherique ("glidarc"): application à la destruction de bactéries du genre *Erwinia* (in French) ["Bacterial inactivation by glidarc discharge : application to the destruction of *Erwinia* bacteria"], PhD Dissertation, University of Rouen, Rouen, France .

[33] Kamgang Youbi G., Herry J.-M., Bellon -Fontaine M.-N., Brisset J.-L., Doubla A., Naitali M. (2007)- Evidence of Temporal Post-Discharge decontaminationof bacteria by gliding electric discharges: application to *Hafnia alvei*- Appl. Env. Microbiol. 73: 4791-4796.

[34] Lerouge S., Wertheimer M., Marchand R., Tabrizian M., L'Yahia H. (2011)- Effects of gas composition on spore mortality and etching during low pressure plasma sterilization- J. Biomed. Mat. Res. 51: 128-135**.**

[35] Kamgang-Youbi G., Herry J.-M., Meilheuc T., Brisset J.-L., Bellon-Fontaine M.-N., Doubla A.,. Naitali M. (2009)- Microbial inactivation using plasma activated water abtained by gliding electric discharges- Let. Appl. Microbiol.48: 13-18.

[36] Abdelmalek F. private communication.

[37] Kamgang Youbi G., Herry E., Brisset J.-L., Bellon-Fontaine M.-N., Doubla A., Naitali M. (2008)- Impact on disinfection efficiency of cell load and of planktonic/adherent/detached state: case of *Hafnia alvei* inactivation by plasma activated water- Appl. Microbiol. Biotechnol 81: 449-457 .

[38] Miyahara T., Ochiai S., Sato T. (2009)- Interaction mechanism between a post-discharge flow and water surface- EPL 86: 45001**.**

[39] Kamgang Youbi G. (2008) Propriétés reactives en post-décharge temporelle des décharges electriques glissantes dans l'air humide: Application à la degradation de colorants azoiques et à la décontamination microbienne (in French). Ph. Dissertation, University of Rouen (France)**.**

[40] Traylor M., Pavlovich M., Karim S., Hait P., Sakiyama Y., Clark D., Graves D. (2011)- Long term antibacterial efficacy of an air plasma activated water- J. Phys. D -A.P. 44: 472001**.**